A Prediction of the Re-entrant Miscibility Cloud-Curves of Aqueous Solutions of Alkyl Polyoxyethylene Surfactants with the Saft-HS Approach

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Equations of state based on the statistical associating fluid theory (SAFT) for mixtures of associating chain molecules have now been used to examine the phase equilibria of a variety of fluid mixtures of varying molecular complexity. In this contribution, we used a simplified version of the approach (SAFT-HS) to predict the liquid-liquid phase equilibria of aqueous solutions of alkyl polyoxyethylene (C_iE_i) surfactants. The water molecules are modeled as hard spheres with four association sites to treat the hydrogen bonding; the dispersion forces are treated at the van der Waals mean-field level. The surfactant molecules are modeled as chains of hard-sphere segments with two/three bonding sites to treat the terminal hydroxyl group and an additional three sites per oxyethylene group; the dispersion forces are treated as for water. The phase equilibria of aqueous solutions of alkyl polyoxyethylene surfactants are characterized by a so-called cloud-curve which represents the region of liquid-liquid immiscibility of two micellar solutions (one rich and one poor in surfactant). The systems exhibit a lower critical solution temperature (LCST), which denotes the lower limit of immiscibility, and in some cases a complete closed-loop region with an upper critical solution temperature (UCST) corresponding to re-entrant miscibility. In this case the behavior can be explained in terms of the competition between the incompatibility of the water with the alkyl chain and the hydrogen bonding between water and the head groups. For appropriate choices of the intermolecular parameters, the SAFT-HS approach predicts cloud-curves with both a UCST and an LCST. The critical temperatures are in reasonable agreement with the experimental data, as is the extent of immiscibility. We have studied the possibility of the transferability of the intermolecular potentials for different members of the C_iE_i homologous series. Although the general trends are reproduced, slightly different dispersion forces have to be used for the various systems in order to provide quantitative agreement with experiment. This is not altogether surprising for such complex aqueous micellar solutions.